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# **Enhancing Lithium Ion Conductivity in Lithium Superionic Conductor (LISICON) Solid Electrolytes Through a Mixed Polyanion Effect**

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Polyanion Effect

## ABSTRACT

LISICON-related compositions  $\text{Li}_{4\pm x}\text{Si}_{1-x}\text{X}_x\text{O}_4$  ( $\text{X} = \text{P}, \text{Al}, \text{Ge}$ ) are important materials that have been identified as potential solid electrolytes for all solid state batteries. Here we show that the room temperature lithium ion conductivity can be improved by several orders of magnitude through substitution on Si sites. We apply a combined computer simulation and experimental approach to a wide range of compositions:  $\text{Li}_4\text{SiO}_4$ ,  $\text{Li}_{3.75}\text{Si}_{0.75}\text{P}_{0.25}\text{O}_4$ ,  $\text{Li}_{4.25}\text{Si}_{0.75}\text{Al}_{0.25}\text{O}_4$ ,  $\text{Li}_4\text{Al}_{0.33}\text{Si}_{0.33}\text{P}_{0.33}\text{O}_4$  and  $\text{Li}_4\text{Al}_{1/3}\text{Si}_{1/6}\text{Ge}_{1/6}\text{P}_{1/3}\text{O}_4$  which include new doped materials. Depending on the temperature, three different  $\text{Li}^+$  ion diffusion mechanisms are observed. The polyanion mixing introduced by substitution lowers the temperature at which the transition to a superionic state with high  $\text{Li}^+$  ion conductivity occurs. These insights help to rationalize the mechanism of the lithium ion conductivity enhancement and provide strategies for designing materials with promising transport properties.

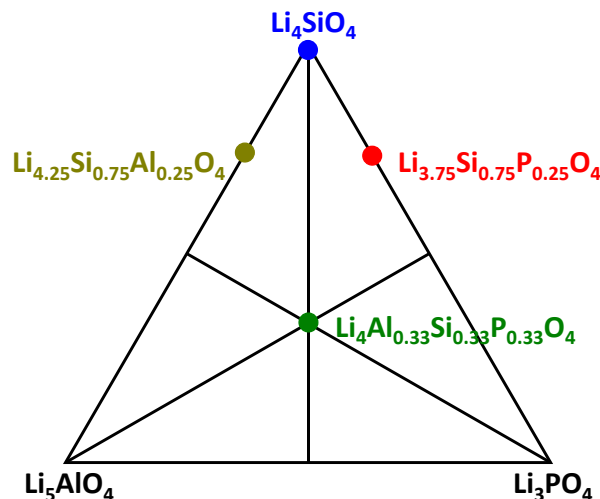
## 1. Introduction

Lithium ion batteries are widely used in electric vehicles and portable devices.<sup>1–5</sup> However, owing to various intrinsic drawbacks of liquid electrolytes (for example, chemical and thermal instability and complex reactions at the solid/liquid interface), other technologies with better performance for specific applications are required. Among various electrochemical energy storage devices, All Solid State Batteries (ASSBs) have been proposed to provide improved chemical and electrochemical stability (wide potential window), greater safety and easier device fabrication.<sup>6–12</sup>

The search for new, stable and highly conducting solid electrolytes has increased significantly in recent years. Considerable research efforts have been carried out in exploring crystal structural families with high ionic conductivity, including the NASICON (e.g.  $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ ),<sup>13–16</sup> LISICON (Lithium Super Ionic CONductor, e.g.  $\gamma\text{-Li}_3\text{PO}_4$ )<sup>17–21</sup> and thio-LISICON,<sup>22–25</sup> garnets (e.g.  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ )<sup>26,27</sup> and related structures.<sup>28–32</sup> Among these structural families, the compositions  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  (10 mS/cm at 25 °C) and  $\text{Li}_{9.54}\text{Si}_{1.74}\text{P}_{1.44}\text{S}_{11.7}\text{Cl}_{0.3}$  (25 mS/cm at 25 °C) reported by Kanno *et al.* present the highest ionic conductivities to date.<sup>6,25</sup> However, sulphide chemistry can be challenging in terms of its high sensitivity to moisture.<sup>33–35</sup> It is believed that the reproducible synthesis of phase pure materials will be a particular issue that will be difficult to overcome. In contrast, oxide-based LISICON materials can be obtained from traditional solid state reactions and present fewer air-sensitivity issues. Previous studies show that the formation of solid solutions (such as  $\text{Li}_{4-x}\text{Si}_{1-x}\text{P}_x\text{O}_4$  or  $\text{Li}_{4+x}\text{Si}_{1-x}\text{Al}_x\text{O}_4$ ) can significantly improve the ionic conductivity.<sup>20,36–42</sup> However, there is limited work on additional doping of these LISICON systems.

The mechanism for such drastic enhancement of conductivity in the solid solution compositions is considered to be caused by the increased concentration of defects which act as charge carriers. Our previous work revealed an interstitialcy or knock-on type mechanism in the case of lithium ion diffusion in  $\text{Li}_{3.5}\text{Si}_{0.5}\text{P}_{0.5}\text{O}_4$  at 573 K.<sup>20</sup> However, the influence of the polyanion groups (e.g.  $\text{SiO}_4$ ,  $\text{PO}_4$ ) has not been discussed in detail. In particular, there is limited work on compositions with more than two types of polyanion groups. For the composition  $\text{Li}_{4.25}\text{Si}_{0.75}\text{Al}_{0.25}\text{O}_4$ , previous work has reported that this material crystallizes in a LISICON structure.<sup>43</sup> However, detailed crystallographic information, e.g. Li atomic positions and site occupancy, is still lacking. For  $\text{Li}_4\text{Al}_{0.33}\text{Si}_{0.33}\text{P}_{0.33}\text{O}_4$ , to the best of our knowledge, no previous synthesis and characterisation work has been reported. Such crystal structural information is important to aid understanding of ion diffusion mechanisms at the atomistic scale.

In this study, we investigate the temperature dependence of the crystal structure and the ion diffusion mechanism and whether the co-existence of various  $\text{XO}_4$  tetrahedra ( $(\text{SiO}_4)^{4-}$ ,  $(\text{PO}_4)^{3-}$  and  $(\text{AlO}_4)^{5-}$ ) within a given structure leads to lower lithium ion transport barriers similar to the ‘mixed anion effect’ reported in polymer and glass-ceramic systems.<sup>44–47</sup> We have synthesized, characterised and modelled a series of compositions ( $\text{Li}_4\text{SiO}_4$ ,  $\text{Li}_{3.75}\text{Si}_{0.75}\text{P}_{0.25}\text{O}_4$ ,  $\text{Li}_{4.25}\text{Si}_{0.75}\text{Al}_{0.25}\text{O}_4$ ,  $\text{Li}_4\text{Al}_{0.33}\text{Si}_{0.33}\text{P}_{0.33}\text{O}_4$  and  $\text{Li}_4\text{Al}_{1/3}\text{Si}_{1/6}\text{Ge}_{1/6}\text{P}_{1/3}\text{O}_4$ ) which are formed through cationic substitution on the  $\text{Si}^{4+}$  site of the parent LISICON-like  $\text{Li}_4\text{SiO}_4$  structure (see Figure 1 for compositional relations).



**Figure 1.** Phase diagram showing the compositions studied ( $\text{Li}_4\text{SiO}_4$  (blue),  $\text{Li}_{3.75}\text{Si}_{0.75}\text{P}_{0.25}\text{O}_4$  (red),  $\text{Li}_{4.25}\text{Si}_{0.75}\text{Al}_{0.25}\text{O}_4$  (dark yellow),  $\text{Li}_4\text{Al}_{0.33}\text{Si}_{0.33}\text{P}_{0.33}\text{O}_4$  (green)) and their relation to the three parent compositions ( $\text{Li}_4\text{SiO}_4$ ,  $\text{Li}_5\text{AlO}_4$  and  $\text{Li}_3\text{PO}_4$ ).

This work represents to our knowledge the first successful doping of more than three elements on the silicon site and the first application of van Hove analysis of these systems, which sheds new light on the nature of the superionic transition in LISICON materials. The findings here are directly transferrable to the high conductivity sulphide-based thio-LISICON systems and offer design strategies to further improve the conductivity.

## 2. Methods

### 2.1 Synthesis, structural and chemical characterization

$\text{Li}_4\text{SiO}_4$ ,  $\text{Li}_{3.75}\text{Si}_{0.75}\text{P}_{0.25}\text{O}_4$ ,  $\text{Li}_{4.25}\text{Si}_{0.75}\text{Al}_{0.25}\text{O}_4$  and  $\text{Li}_4\text{Al}_{0.33}\text{Si}_{0.33}\text{P}_{0.33}\text{O}_4$  were synthesized by solid state reactions at  $800^\circ\text{C}$ . Stoichiometric raw materials ( $\text{LiOH}\cdot\text{H}_2\text{O}$ , fumed  $\text{SiO}_2$ ,  $\beta\text{-Li}_3\text{PO}_4$ ,

Al(OH)<sub>3</sub>) were first ball milled (zirconia beads/powder = 12/1 in mass, 600 rpm, 12 hours) in zirconia jars. The as-homogenized mixture was then cold-pressed into pellets and heated at 800°C for 12 hours under Ar flow, followed by slow cooling to 298 K and then grinded. The Si/Al/P relative concentrations in the powder were confirmed by Energy Dispersed X-ray (EDX) analysis. The crystal structure of these samples was studied by powder X-ray diffraction. Neutron powder diffraction patterns were collected for Li<sub>4</sub>SiO<sub>4</sub>, Li<sub>3.75</sub>Si<sub>0.75</sub>P<sub>0.25</sub>O<sub>4</sub> and Li<sub>4.25</sub>Si<sub>0.75</sub>Al<sub>0.25</sub>O<sub>4</sub> using the high-resolution D2B diffractometer at ILL (Institute Laue-Langevin, Grenoble, France). The ionic conductivity values were measured using pellet samples fabricated by Spark Plasma Sintering process (700 °C, 30 minutes) followed by gold sputtering on each plane surface. AC Electrical Impedance Spectroscopy (EIS) measurements were performed under argon to avoid moisture at various stabilized temperatures ranging from 50 to 300 °C (upon heating and cooling with a step of 25 °C) using a Bio-Logic MTZ-35 Impedance Analyzer, in a frequency range of 30 MHz to 0.1 Hz and with an excitation voltage of 0.1 V. From the Nyquist plots of the complex impedance data, the lithium ionic conductivities of the samples were derived.

## 2.2 Atomistic modeling

Atomistic potentials-based methods were used and are detailed elsewhere;<sup>48,49</sup> hence only a brief overview is presented here. Molecular dynamics (MD) simulation of ion diffusion was performed with the LAMMPS code.<sup>50,51</sup> The interatomic potentials we used here include a long-range Coulomb term, a short-range Morse function and a repulsive contribution. The parameters were taken from the extensive library of potentials developed by Pedone *et al.*,<sup>52</sup> which have been shown to perform well in MD simulations of silicates and polyanion-type materials. The mathematical

form of the potentials and the values of the parameters are listed in Supplementary Information S1. Based on the crystal structure we determined from single crystal X-ray diffraction and powder neutron diffraction, a supercell containing about 6,000 atoms was generated. MD simulations were performed for long timescales ( $\sim 3$  ns) with a time step of 0.002 ps at a wide range of temperatures (473 to 1173 K). The mean squared displacement (*MSD*) of  $\text{Li}^+$  ions was resolved and the chemical diffusion coefficients (*D<sub>c</sub>*) were then calculated from the relation:  $D_c = \frac{1}{6} \frac{d\langle \text{MSD} \rangle}{dt}$ . The tracer diffusion coefficients (*D<sub>t</sub>*) were derived in a similar way using the mean displacement squared (*MDS*). The ionic conductivities were then calculated according to the Nernst-Einstein equation:

$$\frac{\sigma}{D_c} = \frac{nq^2}{fkT} \quad (1)$$

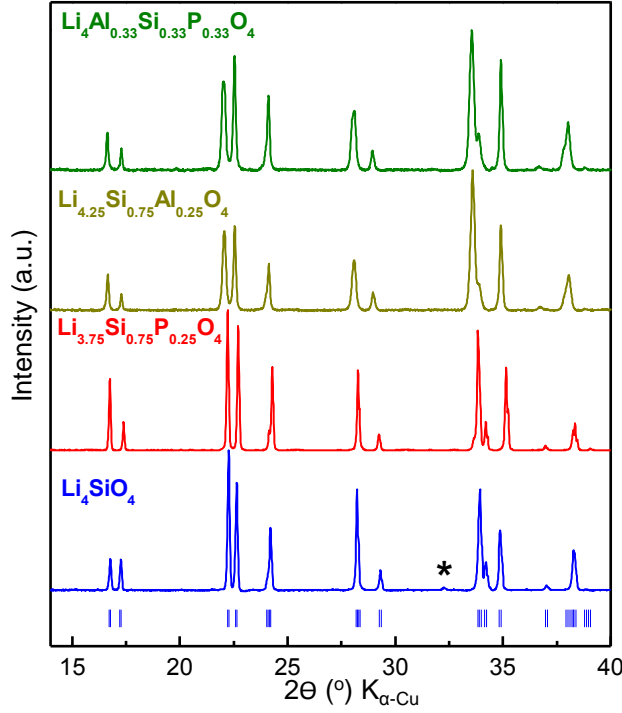
in which *f* is the Haven Ratio defined as the ratio of *D<sub>c</sub>* over *D<sub>t</sub>* (their values are listed in the Supporting Information), *n* is the density of charge carrier (number of  $\text{Li}^+$  ions per volume unit), *q* is the charge, *k* is the Boltzmann constant and *T* is the system temperature. Such atomistic modeling techniques have been applied successfully to a range of lithium (and sodium) battery materials.<sup>53–</sup>

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### 3. Results and discussion

#### 3.1 Crystal structure of the LISICON-like materials





**Figure 2.** X-ray powder diffraction patterns for  $\text{Li}_4\text{SiO}_4$  (blue),  $\text{Li}_{3.75}\text{Si}_{0.75}\text{P}_{0.25}\text{O}_4$  (red),  $\text{Li}_{4.25}\text{Si}_{0.75}\text{Al}_{0.25}\text{O}_4$  (dark yellow) and  $\text{Li}_4\text{Al}_{0.33}\text{Si}_{0.33}\text{P}_{0.33}\text{O}_4$  (green). The Bragg positions of  $\text{Li}_4\text{SiO}_4$  (sub-cell model) are shown in blue bars. (\*: superstructure reflexion)

The crystal structures of  $\text{Li}_4\text{SiO}_4$ ,  $\text{Li}_{3.75}\text{Si}_{0.75}\text{P}_{0.25}\text{O}_4$ ,  $\text{Li}_{4.25}\text{Si}_{0.75}\text{Al}_{0.25}\text{O}_4$  and  $\text{Li}_4\text{Al}_{0.33}\text{Si}_{0.33}\text{P}_{0.33}\text{O}_4$  have been investigated using powder X-ray diffraction. The obtained diffraction patterns for the four samples are shown in Figure 2.

All these four samples are well crystallized and single phase. It is known that  $\text{Li}_4\text{SiO}_4$  crystallizes in a monoclinic ‘supercell’ (space group  $P2_1/m$ , no.11) with  $Z=14$  at 298 K and undergoes a phase transition to a ‘sub-cell’ with  $Z=2$  at temperatures higher than 750 K.<sup>20,59,60</sup> This transition is due to a disordering within the  $\text{Li}^+$  crystallographic positions. This order-disorder transition in the  $\text{Li}^+$  ion positions suggests that the diffusion mechanism may change with temperature. In contrast, the crystal structures at 298 K of the substituted compositions  $\text{Li}_{3.75}\text{Si}_{0.75}\text{P}_{0.25}\text{O}_4$ ,  $\text{Li}_{4.25}\text{Si}_{0.75}\text{Al}_{0.25}\text{O}_4$

and  $\text{Li}_4\text{Al}_{0.33}\text{Si}_{0.33}\text{P}_{0.33}\text{O}_4$  can be described using the ‘sub-cell’ model. The cell parameters obtained through full pattern profile matching are listed in Table 1.

**Table 1.** Cell parameters of  $\text{Li}_4\text{SiO}_4$ ,  $\text{Li}_{3.75}\text{Si}_{0.75}\text{P}_{0.25}\text{O}_4$ ,  $\text{Li}_{4.25}\text{Si}_{0.75}\text{Al}_{0.25}\text{O}_4$  and  $\text{Li}_4\text{Al}_{0.33}\text{Si}_{0.33}\text{P}_{0.33}\text{O}_4$  obtained from full pattern profile matching of X-ray powder diffraction data.

	$\text{Li}_4\text{SiO}_4$	$\text{Li}_{3.75}\text{Si}_{0.75}\text{P}_{0.25}\text{O}_4$	$\text{Li}_{4.25}\text{Si}_{0.75}\text{Al}_{0.25}\text{O}_4$	$\text{Li}_4\text{Al}_{0.33}\text{Si}_{0.33}\text{P}_{0.33}\text{O}_4$
$a$ (Å)	5.1497(2)	5.10836(7)	5.1496(2)	5.1475(3)
$b$ (Å)	6.1001(2)	6.1126(2)	6.1771(4)	6.1779(5)
$c$ (Å)	5.2981(2)	5.3020(2)	5.3424(2)	5.3497(3)
$\beta$ (deg)	90.316(2)	90.343(2)	90.297(3)	90.335(3)
$V/Z$ (Å <sup>3</sup> )	83.214(4)	82.776(3)	84.968(6)	85.061(9)

The crystal structures can be described as isolated polyanionic tetrahedra ( $\text{SiO}_4$ ,  $\text{PO}_4$ ) connected to  $\text{LiO}_n$  ( $n=4, 5$  and  $6$ ) polyhedra through corner and/or edge sharing. For  $\text{Li}_4\text{SiO}_4$  and  $\text{Li}_{3.75}\text{Si}_{0.75}\text{P}_{0.25}\text{O}_4$ , detailed structural descriptions were reported in previous studies.<sup>20,61</sup> In  $\text{Li}_{3.75}\text{Si}_{0.75}\text{P}_{0.25}\text{O}_4$ , the Si and P atoms share the same crystallographic sites and  $(\text{SiO}_4)^{4-}$  and  $(\text{PO}_4)^{3-}$  coexist in a disordered manner.

To the best of our knowledge, no investigation for the crystal structure of  $\text{Li}_{4.25}\text{Si}_{0.75}\text{Al}_{0.25}\text{O}_4$  has been reported in the past. Ortiz-Landeros *et al.*<sup>43</sup> have only stated that  $\text{Li}_{4+x}\text{Si}_{1-x}\text{Al}_x\text{O}_4$  ( $0 \leq x \leq 0.5$ ) compositions show very similar X-ray diffraction pattern to that of  $\text{Li}_4\text{SiO}_4$ . In this work we have carried out powder neutron diffraction and single crystal X-ray diffraction for  $\text{Li}_{4.25}\text{Si}_{0.75}\text{Al}_{0.25}\text{O}_4$ . The refinement results of the crystal structure are listed in the Supplementary

Information. From neutron diffraction data, the refined lithium amount is 4.1(3) per formula. The crystal structure of  $\text{Li}_{4.25}\text{Si}_{0.75}\text{Al}_{0.25}\text{O}_4$  is very similar to that of  $\text{Li}_{3.75}\text{Si}_{0.75}\text{P}_{0.25}\text{O}_4$ ,<sup>20</sup> with a unit cell containing two  $\text{XO}_4$  tetrahedra and similar distribution of lithium crystallographic sites. Each X site is statistically shared by 0.75 Si and 0.25 Al atoms. In the mixed  $\text{XO}_4$  group, the average X-O bond length is 1.690 Å, which is very close to the value of 1.684 Å obtained by linear interpolation between the average Si-O distance in  $\text{Li}_4\text{SiO}_4$  (1.641 Å) and Al-O distance in  $\beta\text{-Li}_5\text{AlO}_4$  (1.814 Å) as reported by Hoppe *et al.*<sup>62</sup> This is a strong indication that the experimental Si/Al stoichiometry of the powder is very close to the nominal one and that the structural model that we are using is valid.

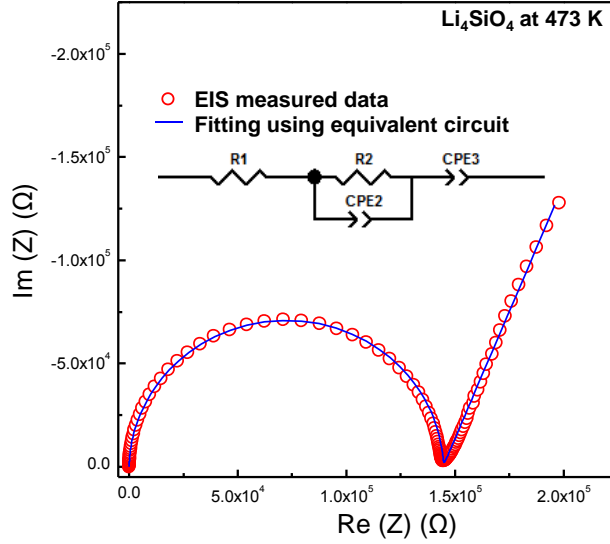
### 3.2 Ionic conductivity enhancement by mixing tetrahedral groups

The ionic conductivity of each material has been measured by EIS technique as a function of temperature. Figure 3 shows a typical Nyquist plot obtained for  $\text{Li}_4\text{SiO}_4$  at 473 K.

A semi-circle can be observed at high frequencies, which can be attributed to the solid electrolyte lithium ion conduction. The spectra were fitted by an equivalent circuit (insert in Figure. 3) composed by an initial resistor R1 (for the device and current collectors resistance) in series with one resistor R2 (for solid electrolyte resistance) in parallel with a constant phase element CPE2 (for the non-ideal capacitance between particles) and in series with another CPE3 (for the impedance of both the top and bottom electrode-electrolyte junctions). The ionic conductivity  $\sigma$  was then calculated using the equation:

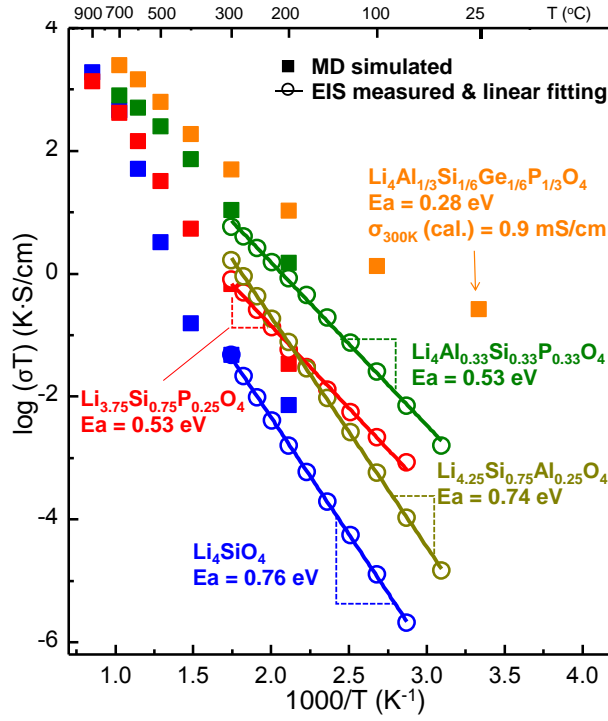
$$\sigma = \frac{h}{RS} \quad (2)$$

in which  $h$  is the thickness of the solid electrolyte pellet,  $S$  the pellet surface and  $R$  the resistance obtained from the fitted  $R2$  value. A fast reduction of the semi-circle diameter is noticed upon heating, in line with the enhancement of the ionic conductivity with temperature.



**Figure 3.** Nyquist plot for EIS measured data (red circles) and fitted curve (blue line) using the inserted equivalent circuit. The curve is obtained from measuring a  $\text{Li}_4\text{SiO}_4$  pellet ( $h = 1.60$  mm and  $S = 26.75$  mm<sup>2</sup>) at 473 K. The fitting was performed using the ZView software.

The ionic conductivities have also been calculated using the MD method described in detail in the ‘Methods’ section. In Figure 4 the experimental and MD simulated ionic conductivity values of  $\text{Li}_4\text{SiO}_4$ ,  $\text{Li}_{3.75}\text{Si}_{0.75}\text{P}_{0.25}\text{O}_4$ ,  $\text{Li}_{4.25}\text{Si}_{0.75}\text{Al}_{0.25}\text{O}_4$ ,  $\text{Li}_4\text{Al}_{0.33}\text{Si}_{0.33}\text{P}_{0.33}\text{O}_4$  and  $\text{Li}_4\text{Al}_{1/3}\text{Si}_{1/6}\text{Ge}_{1/6}\text{P}_{1/3}\text{O}_4$  are plotted in the form of  $\log(\sigma T)$  as a function of  $1000/T$ .



**Figure 4.**  $\text{Li}^+$  ionic conductivity ( $\sigma$ ) Arrhenius plots for  $\text{Li}_4\text{SiO}_4$  (blue),  $\text{Li}_{3.75}\text{Si}_{0.75}\text{P}_{0.25}\text{O}_4$  (red),  $\text{Li}_{4.25}\text{Si}_{0.75}\text{Al}_{0.25}\text{O}_4$  (dark yellow),  $\text{Li}_4\text{Al}_{0.33}\text{Si}_{0.33}\text{P}_{0.33}\text{O}_4$  (green) and  $\text{Li}_4\text{Al}_{1/3}\text{Si}_{1/6}\text{Ge}_{1/6}\text{P}_{1/3}\text{O}_4$  (orange). MD simulated values are shown in solid squares. Conductivity values deduced from EIS measurements are shown in circles. Linear fits for experimental values are plotted in solid lines. The activation energies are derived in the temperature range of 50 to 300 °C.

For each composition, the EIS measured and the MD simulated ionic conductivity values are in good agreement and follow the expected Arrhenius relationship:

$$\sigma T = A \exp\left(-\frac{Ea}{kT}\right) \quad (3)$$

where  $A$  is a pre-exponential factor related to charge carrier concentration and  $Ea$  is the activation energy.  $\text{Li}_4\text{SiO}_4$  shows low ionic conductivity in the common solid state battery working temperature range (RT to 473 K, with  $\sigma_{473\text{K}} = 4 \cdot 10^{-6}$  S/cm). In both mixed “binary” compositions the ionic conductivity values are increased by two orders of magnitude, with  $\sigma_{473\text{K}} = 1 \cdot 10^{-4}$  S/cm

for  $\text{Li}_{3.75}\text{Si}_{0.75}\text{P}_{0.25}\text{O}_4$  and  $2.10^{-4}$  S/cm for  $\text{Li}_{4.25}\text{Si}_{0.75}\text{Al}_{0.25}\text{O}_4$ . A further enhancement of the ionic conductivity is seen in the “ternary” composition  $\text{Li}_4\text{Al}_{0.33}\text{Si}_{0.33}\text{P}_{0.33}\text{O}_4$  with  $\sigma_{473\text{K}} = 1.10^{-3}$  S/cm. These results indicate that substitution on the Si sites (thus creating either Li vacancies or  $\text{Li}^+$  interstitial sites) can effectively promote lithium ion diffusivity. This conclusion is valid not only for the oxide LISICON type materials, but also appears to be applicable for sulphide based solid electrolytes.<sup>25</sup> It is significant that the MD simulated ionic conductivity of  $\text{Li}_4\text{Al}_{1/3}\text{Si}_{1/6}\text{Ge}_{1/6}\text{P}_{1/3}\text{O}_4$  is as high as 0.9 mS/cm at 300 K, which is one of the highest values among oxide-based solid electrolytes.<sup>29,46,63</sup> We notice that the slopes of the data are not strictly linear in the temperature range of 300 to 1173 K, suggesting that the Li diffusion mechanism is temperature dependent. Nevertheless, the non-Arrhenius behaviour is consistent with the order-disorder transition in the  $\text{Li}^+$  ion positions previously observed using diffraction techniques.

We now address the cause of this conductivity enhancement in substituted compositions. All these compositions crystalize in the LISICON-like structure, with isolated tetrahedra and a wide distribution of Li ions on their crystallographic sites. The crystal structure and Li distribution are the same in our MD simulations for these compositions; hence, the influence of structural differences and cation ordering is minimized, which allows us to focus on the effect arising from the mixing of the polyanion groups. In general, the presence of various polyanion groups in the structure improves cation mobility by lowering the energy barrier for  $\text{Li}^+$  migration. A similar phenomenon has been observed in the  $\text{Li}_2\text{S} - \text{GeS}_2 - \text{LiBr} - \text{LiI}$  system<sup>44</sup>: the mixing of  $\text{S}^{2-}$ , I<sup>-</sup> and Br<sup>-</sup> anions lowers the activation energy and improves cation mobility. The mechanism is termed as the ‘mixed anion effect’. As an analogue, the ionic conductivity enhancement in the  $\text{Li}_4\text{SiO}_4$ -related compositions can be termed as ‘mixed polyanion effect’, since the mixing anions are  $\text{XO}_4$  groups.

In order to evaluate the influence of each type of polyanion group, several intrinsic structural and energy characteristics of  $\text{XO}_4$  tetrahedra ( $\text{X} = \text{Al}^{3+}$ ,  $\text{Si}^{4+}$ ,  $\text{Ge}^{4+}$ , and  $\text{P}^{5+}$ ) are listed in Table 2.

**Table 2.** Tetrahedral anion charge  $m$ , X-O distance in  $\text{Li}_m\text{XO}_4$ , X-O dissociation energy values,<sup>64</sup>  $\text{Li}^+ - (\text{XO}_4)^{m-}$  interaction minimum positions for different type of tetrahedra. \* Value not available.

$(\text{XO}_4)^{m-}$	X-O distance (Å)	Molar mass	X-O dissociation energy (eV)	$\text{Li}^+ - (\text{XO}_4)^{m-}$ binding energy (eV)	$\text{Li}^+ - (\text{XO}_4)^{m-}$ equilibrium distance (Å)
$(\text{AlO}_4)^{5-}$	1.814	91	5.03	-6.08	5.2
$(\text{SiO}_4)^{4-}$	1.641	92	*	-5.15	5.1
$(\text{GeO}_4)^{4-}$	1.760	137	6.99	-5.06	5.2
$(\text{PO}_4)^{3-}$	1.520	95	6.17	-4.07	5.0

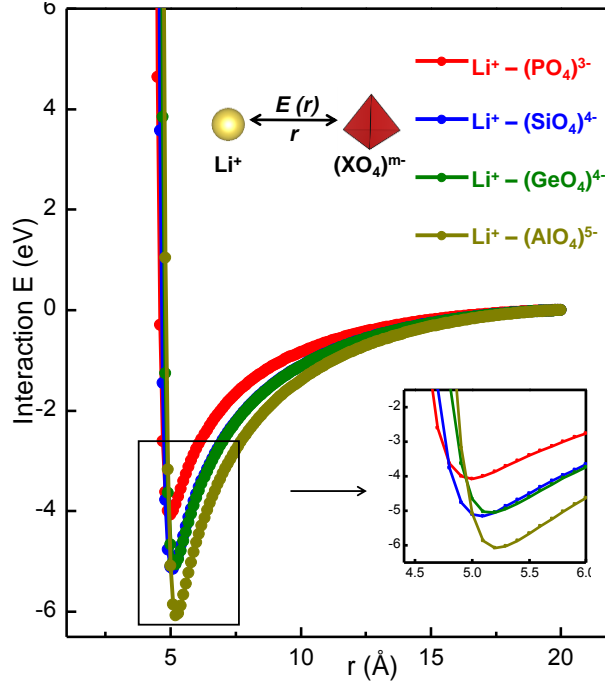
Substitution of silicon can alter the properties of the polyanion groups and the lithium population in three main ways:

1) *Lithium carrier concentration*: the tetrahedral anion charge,  $m$ , will not only influence the interaction between the tetrahedral group and  $\text{Li}^+$  ions, but also the number of charge carriers per formula. For example, with the same amount of substitution (25%) on the Si site,  $\text{Li}_{3.75}\text{Si}_{0.75}\text{P}_{0.25}\text{O}_4$  has 3.75 Li per formula, but  $\text{Li}_{4.25}\text{Si}_{0.75}\text{Al}_{0.25}\text{O}_4$  has 4.25 Li per formula. In Figure 4 we can see that there is no significant difference of ionic conductivities between these two compositions. In comparison to the ionic conductivity values of other compositions, it seems that the variation of the concentration of charge carriers is not the key factor that helps to enhance conductivity values in the substituted compositions.

2) *Polyanion size*: the X-O bond length gives a direct description of the size of the tetrahedra. For consistency, the bond length values listed in Table 2 are taken from the average bond length in the corresponding ortho-oxide: Al-O from  $\beta$ -Li<sub>5</sub>AlO<sub>4</sub> (ICSD-16229),<sup>62</sup> Si-O from Li<sub>4</sub>SiO<sub>4</sub> (ICSD-8222),<sup>60</sup> Ge-O from Li<sub>4</sub>GeO<sub>4</sub> (ICSD-65177) and P-O from  $\gamma$ -Li<sub>3</sub>PO<sub>4</sub> (ICSD-77095). From PO<sub>4</sub> to AlO<sub>4</sub>, the X-O bond length extends by 20%, which gives a 73% expansion of the tetrahedron. In previous studies,<sup>20,24,65–67</sup> the contribution of the tetrahedral motion to the cation ionic conductivity has been discussed, known as the “paddle wheel effect”. The tetrahedra motion is affected by its degree of distortion as well as its rotation. The distortion is represented by the X-O dissociation energy which describes how strong the bond is. The rotation is strongly related to the molar mass of the tetrahedral group. In the study of MD simulation of LGPS,<sup>24</sup> the Li<sup>+</sup> mobility is reported to correlate with a 30° rotation of the GeS<sub>4</sub> and PS<sub>4</sub> groups.

3) *Lithium potential energy surface*: We have calculated the interaction between a Li<sup>+</sup> ion and a (XO<sub>4</sub>)<sup>m-</sup> group. In the calculation one Li<sup>+</sup> ion and one (XO<sub>4</sub>)<sup>m-</sup> group was set in a 40 x 40 x 40 Å lattice. The lattice energy was calculated as a function of separation  $r$  and is plotted in Figure 5 for each (XO<sub>4</sub>)<sup>m-</sup> group. The results illustrate that the interaction between Li<sup>+</sup> and XO<sub>4</sub> can vary considerably in both the depth of the potential well and the equilibrium separation. The minimum energy value  $E_{\min}$ , shows a difference as large as 1 eV between Li<sup>+</sup>-(PO<sub>4</sub>)<sup>3-</sup> and Li<sup>+</sup>-(SiO<sub>4</sub>)<sup>4-</sup> and 2 eV between Li<sup>+</sup>-(PO<sub>4</sub>)<sup>3-</sup> and Li<sup>+</sup>-(AlO<sub>4</sub>)<sup>5-</sup>. The equilibrium separation can vary by 0.25 Å.





**Figure 5.** Simulated interaction between a  $\text{Li}^+$  ion and different  $(\text{XO}_4)^{m-}$  tetrahedral groups. The interaction includes a long-range Coulomb term, a short-range Morse function and a repulsive contribution.

The non-uniform potential wells for different  $\text{Li}^+-(\text{XO}_4)^m$  interactions may modify the overall potential energy surface. In  $\text{Li}_4\text{SiO}_4$  lithium occupies a much more uniform set of potential wells and the activation energy is relatively high (0.76 eV). In the substituted compositions  $\text{Li}_{3.75}\text{Si}_{0.75}\text{P}_{0.25}\text{O}_4$ ,  $\text{Li}_{4.25}\text{Si}_{0.75}\text{Al}_{0.25}\text{O}_4$ ,  $\text{Li}_4\text{Al}_{0.33}\text{Si}_{0.33}\text{P}_{0.33}\text{O}_4$  and  $\text{Li}_4\text{Al}_{1/3}\text{Si}_{1/6}\text{Ge}_{1/6}\text{P}_{1/3}\text{O}_4$ , the mixing of these  $\text{XO}_4$  groups with their non uniform potential wells may result in lower barriers between wells and reduced activation energies in the substituted compositions (0.53 eV for  $\text{Li}_{3.75}\text{Si}_{0.75}\text{P}_{0.25}\text{O}_4$ , 0.74 eV for  $\text{Li}_{4.25}\text{Si}_{0.75}\text{Al}_{0.25}\text{O}_4$  and 0.53 eV for  $\text{Li}_4\text{Al}_{0.33}\text{Si}_{0.33}\text{P}_{0.33}\text{O}_4$  from our EIS measurements). The calculated activation energy of 0.28 eV for  $\text{Li}_4\text{Al}_{1/3}\text{Si}_{1/6}\text{Ge}_{1/6}\text{P}_{1/3}\text{O}_4$  is even lower.

### 3.3 Li<sup>+</sup> diffusion mechanism

To understand how the mixing of polyanion groups with different sizes and binding energies to Li<sup>+</sup> affects the conduction mechanisms we have performed statistical analysis of the lithium diffusion. In our previous study,<sup>20</sup> we showed that at 573 K Li<sup>+</sup> diffusion in Li<sub>4</sub>SiO<sub>4</sub> progresses via isolated Li<sup>+</sup> hops with a low conductivity of around 10<sup>-6</sup> S/cm. By contrast, the substituted composition Li<sub>3.5</sub>Si<sub>0.5</sub>P<sub>0.5</sub>O<sub>4</sub> displayed three orders of magnitude higher conductivity (10<sup>-3</sup> S/cm) at the same temperature with Li<sup>+</sup> diffusion occurring via highly correlated motion. To further quantify these changes in diffusive behaviour, we have calculated and plotted the van Hove correlation functions for Li<sub>4</sub>SiO<sub>4</sub>, Li<sub>3.75</sub>Si<sub>0.75</sub>P<sub>0.25</sub>O<sub>4</sub> and Li<sub>4</sub>Al<sub>1/3</sub>Si<sub>1/6</sub>Ge<sub>1/6</sub>P<sub>1/3</sub>O<sub>4</sub> using trajectories obtained from our MD simulations, which can be split into the self-part  $G_s$  and the distinct-part  $G_d$  as follows:

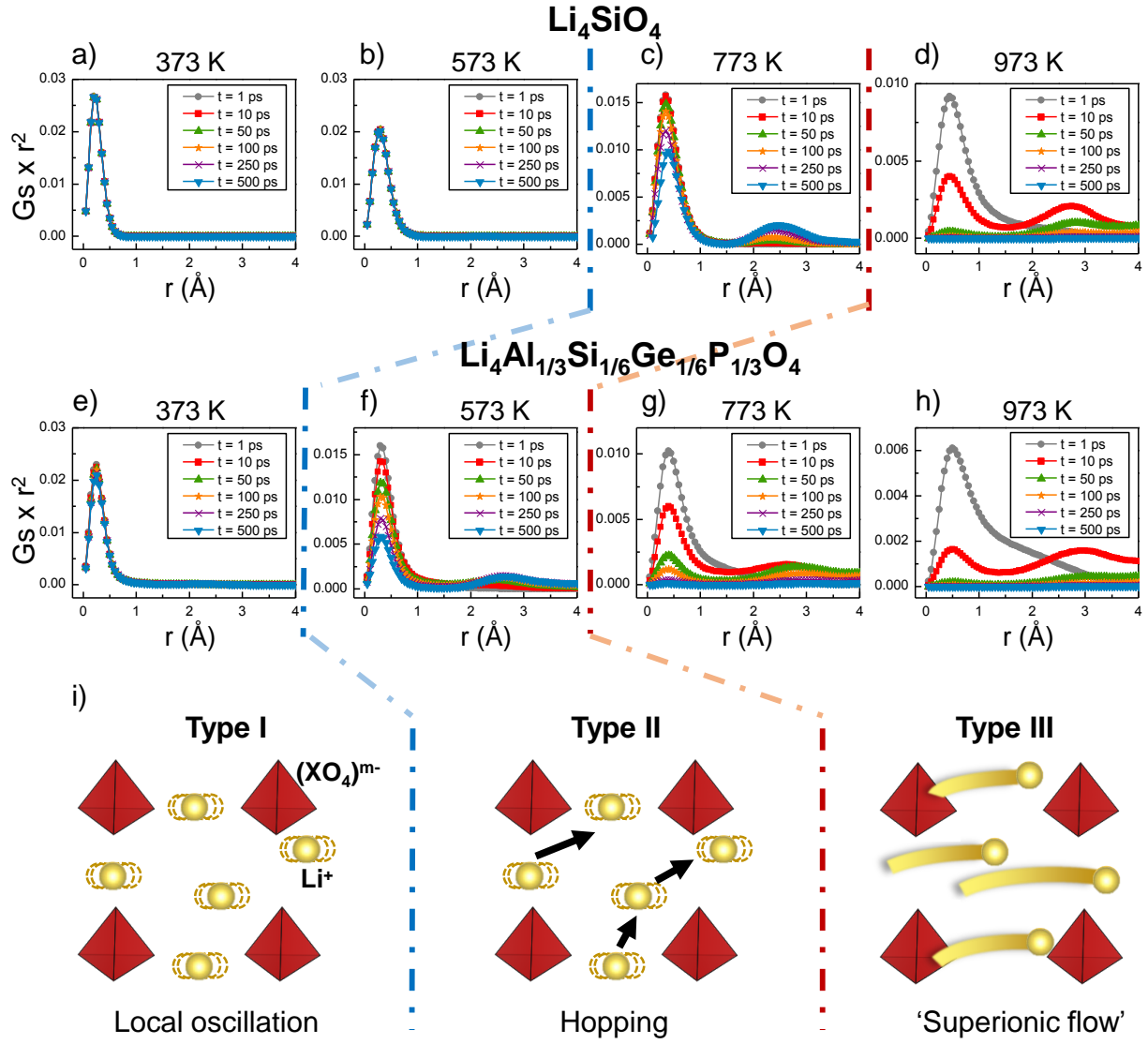
$$G_s(r, t) = \frac{1}{4\pi r^2 N} \left\langle \sum_{i=1}^N \delta[r - |r_i(t_0) - r_i(t + t_0)|] \right\rangle_{t_0} \quad (4)$$

$$G_d(r, t) = \frac{1}{4\pi r^2 N} \left\langle \sum_{i \neq j}^N \delta[r - |r_i(t_0) - r_j(t + t_0)|] \right\rangle_{t_0} \quad (5)$$

In these two equations, the self-part  $G_s$  and the distinct-part  $G_d$  are functions of the Li<sup>+</sup>-Li<sup>+</sup> pair distance  $r$  and of the simulation time  $t$ . The angular brackets denote the ensemble average from the initial time  $t_0$ .  $N$  denotes the number of Li<sup>+</sup> ions in the system.  $\delta()$  is the one-dimensional Dirac delta function.  $r_i(t)$  denotes the position of the  $i$ th Li<sup>+</sup> ion at time  $t$ . For a given  $r$  and  $t$ , the self-part  $G_s(r, t)$  or its transformed version  $r^2 G_s(r, t)$  is related to the probability of finding one atom after it travels a distance  $r$  after a time interval of  $t$ ; the distinct-part  $G_d(r, t)$  or its transformed version  $r^2 G_d(r, t)$  compares the positions of a particle to the position of another particle at different time, and it is related to the probability of finding atom  $j$  ( $j \neq i$ ) with a distance  $r$  (compare to the position

of atom  $i$  at  $t_0$ ) after a time interval of  $t$ . In the particular case with  $t=0$ ,  $G_d(r,t)$  is reduced to the static  $\text{Li}^+-\text{Li}^+$  pair distribution function.

The transformed correlation function thus offers a measure of how correlated the motions of  $\text{Li}^+$  ions are. If  $r^2G_s(r,t)$  retains its shape over different time intervals then non-correlated ion hopping is indicated, whereas peak broadening indicates correlated motion, disorder on the  $\text{Li}^+$  sublattice and, in extreme cases, liquid like diffusive behavior. This method has been successfully used to investigate the diffusion mechanism in other ion conducting materials such as  $\text{Na}_3\text{PS}_4$ <sup>68</sup> and garnet type  $\text{Li}_{7-x}\text{La}_3(\text{Zr}_{2-x}\text{Mx})\text{O}_{12}$ ,<sup>69</sup> but has never been applied to LISICON systems. In Figure 6, the transformed version of the self-part,  $r^2G_s(r,t)$ , is plotted as a function of  $r$  for  $\text{Li}_4\text{SiO}_4$  and  $\text{Li}_4\text{Al}_{1/3}\text{Si}_{1/6}\text{Ge}_{1/6}\text{P}_{1/3}\text{O}_4$  at various simulation temperatures (373, 573, 773 and 973 K). (The  $r^2G_s(r,t)$  for  $\text{Li}_{3.75}\text{Si}_{0.75}\text{P}_{0.25}\text{O}_4$  and the  $r^2G_d(r,t)$  for the three compositions can be found in Supplementary Information.) For each temperature, six time interval values,  $t = 1, 10, 50, 100, 250$  and 500 ps, have been chosen to investigate the structural dynamics evolution. From these simulated data we can classify three distinct types of diffusive behavior according to the shape of  $r^2G_s(r,t)=f(r)$  and  $r^2G_s(r,t)=g(r)$ .



**Figure 6.** Transformed version of the self-part of the van Hove correlation function,  $r^2 G_s(r, t)$  for  $\text{Li}_4\text{SiO}_4$  (a), b), c), and d)) and  $\text{Li}_4\text{Al}_{1/3}\text{Si}_{1/6}\text{Ge}_{1/6}\text{P}_{1/3}\text{O}_4$  (e), f), g), h)) at (from left to right) 373, 573, 773 and 973 K. For each temperature, six curves for  $t = 1, 10, 50, 100, 250$  and  $500$  ps are plotted. At each temperature, the six curves indicate one of the three mechanism types as shown in i).  $\text{Li}^+$  ions are shown in yellow,  $\text{XO}_4$  groups are shown in red.

**Type I - Local Oscillation:**  $\text{Li}_4\text{SiO}_4$  at 373 K (Figure 6a)) and 573 K (Figure 6b)) and  $\text{Li}_4\text{Al}_{1/3}\text{Si}_{1/6}\text{Ge}_{1/6}\text{P}_{1/3}\text{O}_4$  at 373 K (Figure 6e)): the calculated data show only one peak appearing between 0 and 0.5 Å. This peak suggests a high probability of finding lithium ions with this

displacement value; this probability shows weak time dependence. Such a correlation function is typical of atomic vibrations around equilibrium positions. This finding is in good agreement with the result found in the density plot of MD simulations in our previous work.<sup>20</sup> This peak also appears in the other plots of Figure 6 (and listed in Table 3). As the temperature increases, a right shift of the peak position is observed, which is in agreement with the fact that the  $\text{Li}^+$  ions have higher thermal energy at higher temperature.

**Table 3.** First peak position in the self-part of the van Hove correlation function

	373 K	573 K	773 K	973 K
$\text{Li}_4\text{SiO}_4$	0.20 Å	0.30 Å	0.35 Å	0.45 Å
$\text{Li}_4\text{Al}_{1/3}\text{Si}_{1/6}\text{Ge}_{1/6}\text{P}_{1/3}\text{O}_4$	0.25 Å	0.30 Å	0.40 Å	0.50 Å

At each temperature, the peak position for  $\text{Li}_4\text{Al}_{1/3}\text{Si}_{1/6}\text{Ge}_{1/6}\text{P}_{1/3}\text{O}_4$  appears at slightly larger  $r$  value than for  $\text{Li}_4\text{SiO}_4$ , indicating that the motion of  $\text{Li}^+$  ions is less constricted. The mechanism of  $\text{Li}^+$  ion dynamics in these cases can be considered as a local oscillation.

**Type II - Ion Hopping:** For  $\text{Li}_4\text{SiO}_4$  at 773 K (Figure 6c)) and  $\text{Li}_4\text{Al}_{1/3}\text{Si}_{1/6}\text{Ge}_{1/6}\text{P}_{1/3}\text{O}_4$  at 573 K (Figure 6f)), the intensity of the probability peak around 0.40 Å decreases with the evolution of the simulation time. Therefore the probability of finding a  $\text{Li}^+$  ion around its equilibrium position is reduced, indicating that  $\text{Li}^+$  ions have left their original position and migrated to other sites. Another feature in these Type II plots is the presence of a second peak at around  $r = 2.4$  Å, which is the distance between a  $\text{Li}^+$  ion and its closest  $\text{Li}^+$  site in the lattice (varying from 1.8 to 2.9 Å). The appearance of this peak is the signal for  $\text{Li}^+$  ion jumping to its neighboring site and staying on

that site for a certain residual time. Similar to the peak at 0.40 Å, this peak is also time dependent, but its intensity increases with the measurement interval. Over timescales greater than ~100ps sufficient Li<sup>+</sup> hops occur to give an appreciable probability of finding a Li<sup>+</sup> ion on its neighboring site. The hopping can also be seen in the distinct-part of the van Hove correlation function (see Supplementary Information). In the distinct-part curve, there is a peak locating at around 0.4 Å, suggesting the lithium sites are occupied by a new Li<sup>+</sup> ion other than the one at  $t=0$ . These features suggest that Li<sup>+</sup> ion diffusion undergoes hopping mechanism in the Type II conditions.

**Type III - Correlated Superionic Flow:** Li<sub>4</sub>SiO<sub>4</sub> at 973 K (Figure 6d) and Li<sub>4</sub>Al<sub>1/3</sub>Si<sub>1/6</sub>Ge<sub>1/6</sub>P<sub>1/3</sub>O<sub>4</sub> at 773 K (Figure 6g) and 973 K (Figure 6h): in these Type III plots, those curves at  $t = 1$  ps have similar shapes as those in the Type I. However, the intensity of the peak is much weaker (it should be noticed that the scales of the vertical axis are not same), indicating a lower probability of finding a Li<sup>+</sup> ion around its original position. The peak has a large tail, showing that some of the Li<sup>+</sup> ions are displaced for distances larger than 1.5 Å in 1 ps. The curves at  $t = 10$  ps are similar to those in the Type II, with a relatively low intensity peak at 0.4 Å and a broad peak at 2.8 Å, suggesting that in these conditions 10 ps is long enough for a Li<sup>+</sup> ion diffusing to its neighboring site. As the simulation time goes above 100 ps, no other significant peaks can be observed in these plots. This data shows that at high temperatures a significant disordering of the Li<sup>+</sup> sub-lattice in the structure occurs which leads to a more liquid like distribution of Li<sup>+</sup> ions. The diffusivity of the Li<sup>+</sup> ions at these temperatures is significantly enhanced, leading to the non linear Arrhenius behavior in the conductivity values in Figure 4. The Li<sup>+</sup> dynamics can thus be considered to undergo a phase transition into ‘superionic flow’.

As can be seen from the above discussion, the mechanism of Li<sup>+</sup> ion diffusion in each composition is temperature dependent. From low to high temperature, the mechanism evolves from Type I

local oscillation to Type II isolated hopping and to Type III superionic flow. When the diffusion mechanism changes from local oscillation to isolated hopping or isolated hopping to superionic flow, a faster  $\text{Li}^+$  ion mobility is achieved, thus promoting higher ionic conductivity. The ‘mixed polyanion effect’ causes substituted compositions to show a transition to the next diffusion mechanism type at a much lower temperature than in  $\text{Li}_4\text{SiO}_4$ . For instance,  $\text{Li}_4\text{Al}_{1/3}\text{Si}_{1/6}\text{Ge}_{1/6}\text{P}_{1/3}\text{O}_4$  shows a transition to superionic motion at much lower temperature than  $\text{Li}_4\text{SiO}_4$ , and hence the room temperature conductivity is several orders of magnitude greater. In general, these results indicate the atomic scale origin of the orders of magnitude increase in ionic conductivity observed in substituted LISICON materials.

#### 4. Conclusions

The lithium ion transport properties of a range of compositions ( $\text{Li}_4\text{SiO}_4$ ,  $\text{Li}_{3.75}\text{Si}_{0.75}\text{P}_{0.25}\text{O}_4$ ,  $\text{Li}_{4.25}\text{Si}_{0.75}\text{Al}_{0.25}\text{O}_4$ ,  $\text{Li}_4\text{Al}_{0.33}\text{Si}_{0.33}\text{P}_{0.33}\text{O}_4$  and  $\text{Li}_4\text{Al}_{1/3}\text{Si}_{1/6}\text{Ge}_{1/6}\text{P}_{1/3}\text{O}_4$ ) in the LISICON-type structural family have been investigated using a combination of synthesis, diffraction, impedance and modelling techniques. This includes the first detailed report of the crystal structure including atomic positions and site occupancies of  $\text{Li}_{4.25}\text{Si}_{0.75}\text{Al}_{0.25}\text{O}_4$  and the transport properties of a new composition  $\text{Li}_4\text{Al}_{0.33}\text{Si}_{0.33}\text{P}_{0.33}\text{O}_4$ .

The following main findings emerge from our investigation. First, the ionic conductivity of  $\text{Li}_4\text{SiO}_4$  is not high, but can be enhanced through successful substitution on the  $\text{Si}^{4+}$  site. Such doping leads to a ‘mixed polyanion effect’, which helps to modify the potential energy surface and

decrease the  $\text{Li}^+$  ion conduction barrier. Second, the MD modelling results reveal three temperature-dependent mechanisms for  $\text{Li}^+$  ion diffusion: i) local oscillation at low temperature; ii) isolated hopping at intermediate temperature and iii) superionic motion at high temperature. Moreover, we have shown that the type of mechanism in operation depends on both the temperature and the composition.  $\text{Li}_4\text{Al}_{1/3}\text{Si}_{1/6}\text{Ge}_{1/6}\text{P}_{1/3}\text{O}_4$  shows a transition to superionic motion at a much lower temperature than  $\text{Li}_4\text{SiO}_4$  and hence the room temperature ionic conductivity of 0.9 mS/cm, is several orders of magnitude higher. The results are generally applicable to all materials in the LISICON family which share the same structural motif of Li-rich compounds with isolated polyanion tetrahedra.

These insights are important in helping to rationalize how ionic transport is related to local structure and composition, and to develop new strategies for designing solid electrolyte materials with high ionic conductivity. A future avenue to exploit this effect would be mixed ‘oxysulphide’ compositions where the size difference in tetrahedra would be even greater than in the oxides considered here, although a major challenge presented by such oxysulphides (and by substituted LISICONs in general) is the suppression of phase separation.

## ASSOCIATED CONTENT

**Supporting Information.** Equation and values of parameters used in the interatomic potentials. Self-part of the van-Hove correlation function for  $\text{Li}_{3.75}\text{Si}_{0.75}\text{P}_{0.25}\text{O}_4$ . Distinct-part of the van-Hove correlation function. Single crystal measurement conditions and refinement results. Haven ratio values. Crystallographic data and powder neutron diffraction pattern for  $\text{Li}_{4.25}\text{Si}_{0.75}\text{Al}_{0.25}\text{O}_4$ . This material is available free of charge via the Internet at <http://pubs.acs.org>.



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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. All authors contributed equally.

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